

(12)

**EUROPEAN PATENT APPLICATION**

(21) Application number: 85116162.0

(22) Date of filing: 18.12.85

(51) Int. Cl.<sup>4</sup>: **C 07 C 79/36**

**C 07 C 76/02, C 07 C 121/76**  
**A 01 N 35/06, A 01 N 41/06**  
**A 01 N 41/10, C 07 C 79/46**  
**C 07 C 147/06**

(30) Priority: 20.12.84 US 683900

(43) Date of publication of application:  
02.07.86 Bulletin 86/27

(84) Designated Contracting States:  
AT BE CH DE FR GB IT LI NL SE

(71) Applicant: **STAUFFER CHEMICAL COMPANY**

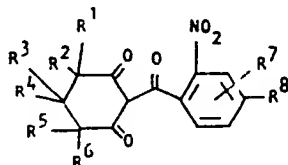
Westport Connecticut 06881(US)

(72) Inventor: **Carter, Charles Garvie**  
1240 Willard Street  
San Francisco Calif. 94117(US)

(74) Representative: **Kraus, Walter, Dr. et al,**  
**Patentanwälte Kraus, Weisert & Partner**  
Thomas-Wimmer-Ring 15  
D-8000 München 22(DE)

(54) **Certain 2-(2'-nitrobenzoyl)-1,3-cyclohexanediones.**

(57) Compounds of the formula



wherein R<sup>1</sup> is hydrogen or C<sub>1</sub>-C<sub>4</sub> alkyl; R<sup>2</sup> is hydrogen, C<sub>1</sub>-C<sub>4</sub> alkyl or

O

R<sup>a</sup>-O-C-

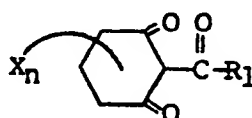
wherein R<sup>a</sup> is C<sub>1</sub>-C<sub>4</sub> alkyl; R<sup>1</sup> and R<sup>2</sup> together are alkylene having 3 to 6 carbon atoms; R<sup>3</sup> is hydrogen or C<sub>1</sub>-C<sub>4</sub> alkyl; R<sup>4</sup> is hydrogen or C<sub>1</sub>-C<sub>4</sub> alkyl; R<sup>5</sup> is hydrogen or C<sub>1</sub>-C<sub>4</sub> alkyl; R<sup>6</sup> is hydrogen or C<sub>1</sub>-C<sub>4</sub> alkyl; and R<sup>7</sup> and R<sup>8</sup> independently are (1) hydrogen; (2) halogen; (3) C<sub>1</sub>-C<sub>4</sub> alkyl; (4) C<sub>1</sub>-C<sub>4</sub> alkoxy; (5) OCF<sub>3</sub>; (6) cyano; (7) nitro; (8) C<sub>1</sub>-C<sub>4</sub> haloalkyl; (9) R<sup>b</sup>SO<sub>n</sub>- wherein n is the integer 0, 1 or 2; and R<sup>b</sup> is (a) C<sub>1</sub>-C<sub>4</sub> alkyl; (b) C<sub>1</sub>-C<sub>4</sub> alkyl substituted with halogen or cyano; (c) phenyl; or (d) benzyl; (10) -NR<sup>c</sup>R<sup>d</sup> wherein R<sup>c</sup> and R<sup>d</sup> independently are

hydrogen or C<sub>1</sub>-C<sub>4</sub> alkyl; (11) R<sup>c</sup>C(O)-wherein R<sup>c</sup> is C<sub>1</sub>-C<sub>4</sub> alkyl or C<sub>1</sub>-C<sub>4</sub> alkoxy; or (12) SO<sub>2</sub>NR<sup>c</sup>R<sup>d</sup> wherein R<sup>c</sup> and R<sup>d</sup> are as defined, with the proviso that R<sup>7</sup> is not attached to the 6-position, are effective as herbicides.

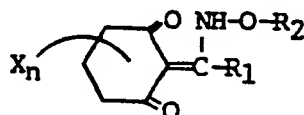
CERTAIN 2-(2'-NITROBENZOYL)-1,3-CYCLOHEXANEDIONES

Background of the Invention

Compounds having the structural formula



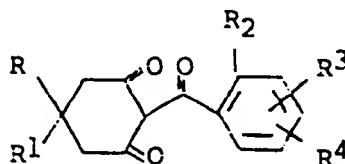
wherein X can be an alkyl, n can be 0, 1, or 2, and R<sub>1</sub> can be phenyl or  
 5 substituted phenyl are described in Japanese Patent Application 84632-1974  
 as being intermediates for the preparation of herbicidal compounds of the  
 formula



wherein R<sub>1</sub>, X, and n are as defined above and R<sub>2</sub> is alkyl, alkenyl, or  
 alkynyl. Specifically taught herbicidal compounds of this latter group  
 10 are those where n is 2, X is 5,5-dimethyl, R<sub>2</sub> is allyl and R<sub>1</sub> is phenyl,  
 4-chlorophenyl or 4-methoxyphenyl.

The precursor intermediates for these three specifically taught  
 compounds have no or almost no herbicidal activity.

European Patent Application No. 83 102 599.4 was published  
 15 October 5, 1983 and relates to certain novel 2-(2-substituted benzoyl)-  
 cyclohexane-1,3-diones as herbicides. The compounds have the following  
 structural formula



wherein R and R<sup>1</sup> are hydrogen or C<sub>1</sub>-C<sub>4</sub> alkyl; R<sup>2</sup> is chlorine, bromine, or iodine; R<sup>3</sup> is hydrogen or halogen; and R<sup>4</sup> is hydrogen, chlorine, bromine, iodine, C<sub>1</sub>-C<sub>4</sub> alkyl, C<sub>1</sub>-C<sub>4</sub> alkoxy, nitro or trifluoromethyl.

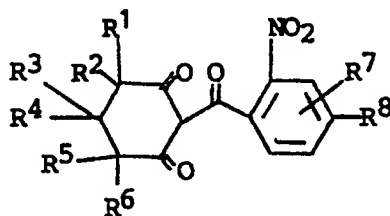
### Description of the Invention

This invention relates to 2-(2-nitrobenzoyl)-1,3-cyclohexane-  
5 diones and their use as herbicides.

The compounds have a nitro substitution in the 2-position of the phenyl moiety of their compounds. The nitro substitution imparts exceptional herbicidal activity to the compounds of this invention.

One embodiment of this invention is an herbicidal composition  
10 comprising an herbicidally active 2-(2-nitrobenzoyl)-1,3-cyclohexanedione and an inert carrier therefor. The 4-, 5- and 6-positions of the 1,3-cyclohexanedione moiety can be substituted, preferably with the groups hereinafter recited. More preferably, the 1,3-cyclohexanedione moiety has no substitution or the 4- or 6-positions are substituted with one or two  
15 methyl groups. The 3-, 4- and 5-positions of the benzoyl moiety can be substituted, preferably with the groups hereinafter recited.

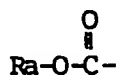
Also embodied within the scope of this invention are novel compounds having the following structural formula



wherein

20 R<sup>1</sup> is hydrogen or C<sub>1</sub>-C<sub>4</sub> alkyl, preferably C<sub>1</sub>-C<sub>2</sub> alkyl, more preferably methyl, most preferably R<sup>1</sup> is hydrogen or methyl;

R<sup>2</sup> is hydrogen; C<sub>1</sub>-C<sub>4</sub> alkyl, preferably C<sub>1</sub>-C<sub>2</sub> alkyl, more preferably methyl or



25 wherein Ra is C<sub>1</sub>-C<sub>4</sub> alkyl, most preferably R<sup>2</sup> is hydrogen or methyl; or R<sup>1</sup> and R<sup>2</sup> together are alkylene having 3 to 6 carbon atoms;

$R^3$  is hydrogen or C<sub>1</sub>-C<sub>4</sub> alkyl, preferably C<sub>1</sub>-C<sub>2</sub> alkyl, more preferably methyl; most preferably  $R^3$  is hydrogen or methyl;

$R^4$  is hydrogen or C<sub>1</sub>-C<sub>4</sub> alkyl, preferably C<sub>1</sub>-C<sub>2</sub> alkyl, more preferably methyl; most preferably  $R^4$  is hydrogen or methyl;

5  $R^5$  is hydrogen or C<sub>1</sub>-C<sub>4</sub> alkyl, preferably C<sub>1</sub>-C<sub>2</sub> alkyl, more preferably methyl; most preferably  $R^5$  is hydrogen or methyl;

$R^6$  is hydrogen or C<sub>1</sub>-C<sub>4</sub> alkyl, preferably C<sub>1</sub>-C<sub>2</sub> alkyl, more preferably methyl, most preferably  $R^6$  is hydrogen;

$R^7$  and  $R^8$  independently are (1) hydrogen; (2) halogen, preferably chlorine, fluorine or bromine; (3) C<sub>1</sub>-C<sub>4</sub> alkyl, preferably methyl; 10 (4) C<sub>1</sub>-C<sub>4</sub> alkoxy, preferably methoxy; (5) OCF<sub>3</sub>; (6) cyano; (7) nitro; (8) C<sub>1</sub>-C<sub>4</sub> haloalkyl, more preferably trifluoromethyl; (9)  $R^bSO_n$ - wherein n is the integer 0, 1 or 2, preferably 2; and

$R^b$  is (a) C<sub>1</sub>-C<sub>4</sub> alkyl, preferably methyl;

15 (b) C<sub>1</sub>-C<sub>4</sub> alkyl substituted with halogen or cyano, preferably chloromethyl, trifluoromethyl or cyanomethyl;

(c) phenyl; or

(d) benzyl;

20 (10)  $-NRC^dR^d$  wherein

$R^c$  and  $R^d$  independently are hydrogen or C<sub>1</sub>-C<sub>4</sub> alkyl;

(11)  $REC(O)-$  wherein

$R^e$  is C<sub>1</sub>-C<sub>4</sub> alkyl or C<sub>1</sub>-C<sub>4</sub> alkoxy; or

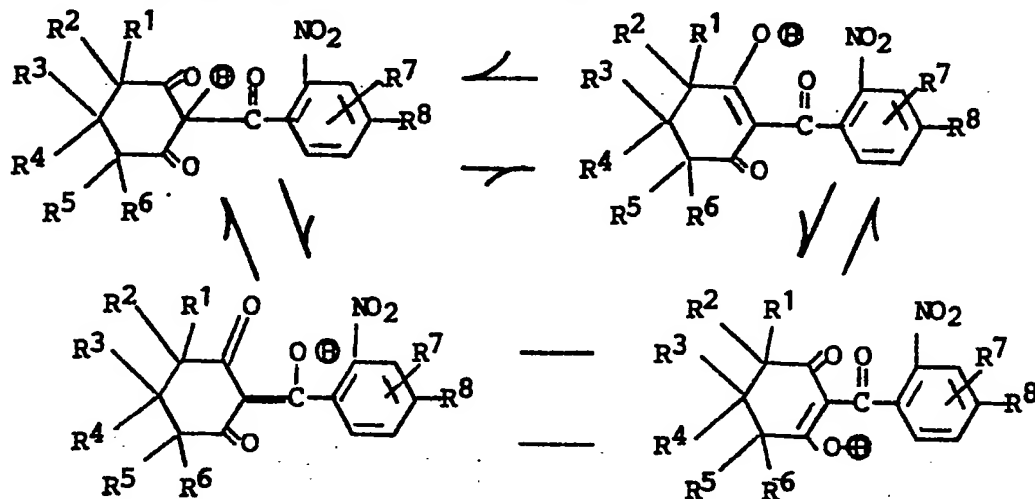
(12)  $-SO_2NRC^dR^d$  wherein  $R^c$  and  $R^d$  are as defined, with the proviso that  $R^7$  25 is not attached to the 6-position.

Preferably,  $R^7$  is in the 3-position. Most preferably  $R^7$  is hydrogen or C<sub>1</sub>-C<sub>4</sub> alkoxy and  $R^8$  is hydrogen, chlorine, bromine, fluorine, CF<sub>3</sub>, or  $R^bSO_2$  wherein  $R^b$  is C<sub>1</sub>-C<sub>4</sub> alkyl, preferably methyl.

The term "C<sub>1</sub>-C<sub>4</sub> alkyl" includes methyl, ethyl, n-propyl, iso- 30 propyl, n-butyl, sec-butyl, isobutyl and t-butyl. The term "halogen" includes chlorine, bromine, iodine and fluorine. The terms "C<sub>1</sub>-C<sub>4</sub> alkoxy" includes methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy, sec-butoxy, isobutoxy and t-butoxy. The term "haloalkyl" includes the eight alkyl groups with one or more hydrogens replaced by chlorine, bromine, iodine or 35 fluorine.

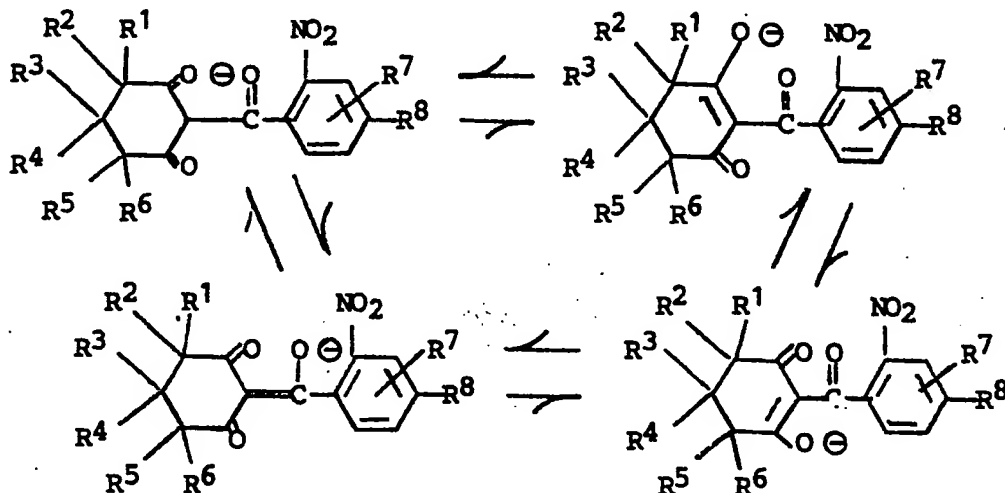
Salts of the above-described compounds (as defined hereinafter) are also the subject of the instant invention.

The compounds of this invention can have the following four structural formulae because of tautomerism:



5 wherein  $R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$ ,  $R^5$ ,  $R^6$ ,  $R^7$  and  $R^8$  are as defined above.

The circled proton on each of the four tautomers is reasonably labile. These protons are acidic and can be removed by any base to give a salt having an anion of the following four resonance forms:



wherein  $R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$ ,  $R^5$ ,  $R^6$ ,  $R^7$  and  $R^8$  are as defined above.

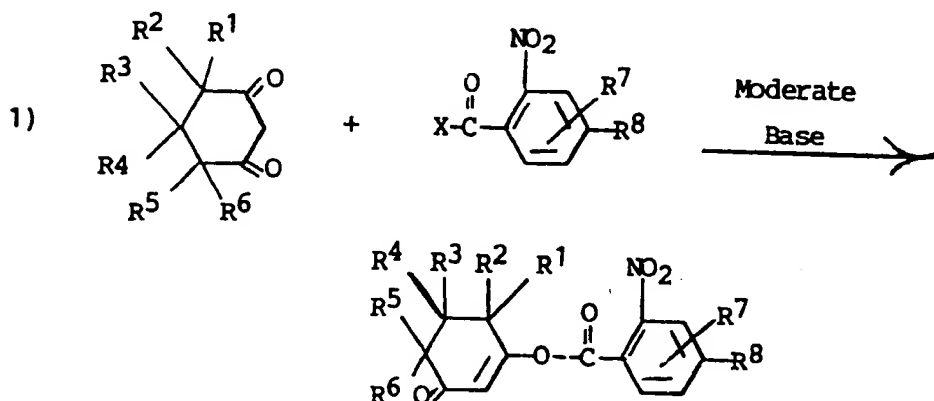
Examples of cations of these bases are inorganic cations such as alkali metals e.g. lithium, sodium, and potassium organic cations such as

substituted ammonium, sulfonium or phosphonium wherein the substituent is an aliphatic or aromatic group.

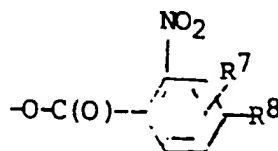
The compounds of this invention and their salts are active herbicides of a general type. That is, they are herbicidally effective against a wide range of plant species. The method of controlling undesirable vegetation of the present invention comprises applying an herbicidally effective amount of the above-described compounds to the area where control is desired.

The compounds of the present invention can be prepared by the following two-step general method.

The process proceeds via the production of an enol ester intermediate as shown in reaction (1). The final product is obtained by rearrangement of the enol ester as shown in reaction (2). The two reactions may be conducted as separate steps by isolation and recovery of the enol ester using conventional techniques prior to conducting step (2), or by addition of a cyanide source to the reaction medium after the formation of the enol ester, or in one step by inclusion of the cyanide source at the start of reaction (1).

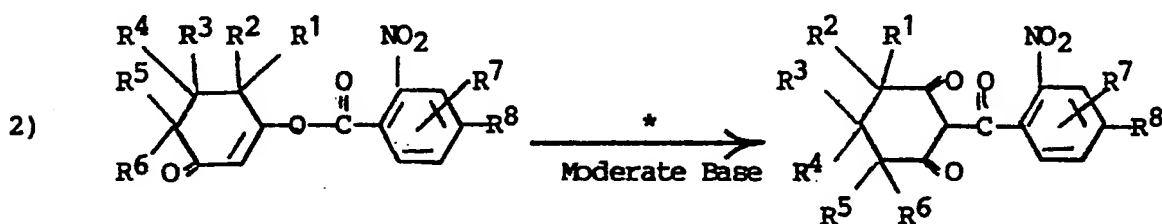


wherein  $R^1$  through  $R^8$  and moderate base are as defined and  $X$  is halogen, preferably chlorine,  $C_1$ - $C_4$  alkyl- $C(O)-O-$ ,  $C_1$ - $C_4$  alkoxy- $C(O)-O-$  or



wherein R<sup>7</sup> and R<sup>8</sup> in this portion of the molecule are identical with those in the reactant shown above and the moderate base is as defined, preferably tri-C<sub>1</sub>-C<sub>6</sub> alkylamine, pyridine, alkali metal carbonate or alkali metal phosphate.

- 5                    Generally, in step (1) mole amounts of the dione and substituted benzoyl reactant are used, along with a mole amount or excess of the base. The two reactants are combined in an organic solvent such as methylene chloride, toluene, ethyl acetate or dimethylformamide. The base or benzoyl reactant preferably are added to the reaction mixture with cooling.
- 10 The mixture is stirred at 0°C-50°C until the reaction is substantially complete.



\* = Cyanide source.

wherein the moderate base and R<sup>1</sup> through R<sup>8</sup> are as defined above.

- Generally, in step (2) a mole of the enol ester intermediate is reacted with 1 to 4 moles of the base, preferably about 2 moles of moderate base and from 0.01 mole to about 0.5 mole or higher, preferably around
- 15 0.1 mole of the cyanide source (e.g., potassium cyanide or acetone cyanohydrin). The mixture is stirred in a reaction pot until the rearrangement is substantially complete at a temperature below 50°C, preferably about 20°C to about 40°C, and the desired product is recovered by conventional
- 20 techniques.

The term "cyanide source" refers to a substance or substances which under the rearrangement conditions consists of or generates hydrogen cyanide and/or cyanide anion.

- The process is conducted in the presence of a catalytic amount
- 25 of a source of cyanide anion and/or hydrogen cyanide, together with a molar excess, with respect to the enol ester, of a moderate base.

Preferred cyanide sources are alkali metal cyanides such as sodium and potassium cyanide; cyanohydrins of methyl alkyl ketones having from 1-4 carbon atoms in the alkyl groups, such as acetone or methyl isobutyl ketone cyanohydrins; cyanohydrins of benzaldehyde or of C<sub>2</sub>-C<sub>5</sub> aliphatic aldehydes such as acetaldehyde, propionaldehyde, etc., cyanohydrins; zinc cyanide; tri(lower alkyl) silyl cyanides, notably trimethyl silyl cyanide; and hydrogen cyanide itself. Hydrogen cyanide is considered most advantageous as it produces relatively rapid reaction and is inexpensive. Among cyanohydrins the preferred cyanide source is acetone cyanohydrin.

The cyanide source is used in an amount up to about 50 mole percent based on the enol ester. It may be used in as little as about 1 mole percent to produce an acceptable rate of reaction at about 40°C on a small scale. Larger scale reactions give more reproducible results with slightly higher catalyst levels of about 2 mole percent. Generally about 1-10 mole % of the cyanide source is preferred.

The process is conducted with a molar excess, with respect to the enol ester, of a moderate base. By the term "moderate base" is meant a substance which acts as a base yet whose strength or activity as a base lies between that of strong bases such as hydroxides (which could cause hydrolysis of the enol ester) and that of weak bases such as bicarbonates (which would not function effectively). Moderate bases suitable for use in this embodiment include both organic bases such as tertiary amines and inorganic bases such as alkali metal carbonates and phosphates. Suitable tertiary amines include trialkylamines such as triethylamine, trialkanolamines such as triethanolamine, and pyridine. Suitable inorganic bases include potassium carbonate and trisodium phosphate.

The base is used in an amount of from about 1 to about 4 moles per mole of enol ester, preferably about 2 moles per mole.

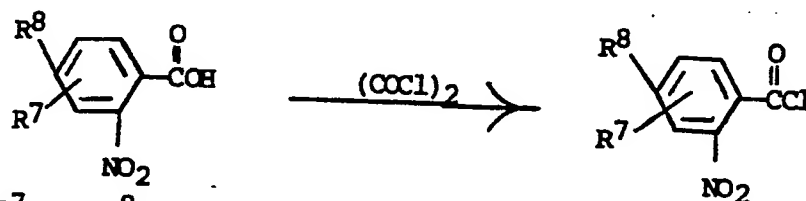
When the cyanide source is an alkali metal cyanide, particularly potassium cyanide, a phase transfer catalyst may be included in the reaction. Particularly suitable phase transfer catalysts are the Crown ethers.



A number of different solvents may be usable in this process, depending on the nature of the acid chloride or the acylated product. A preferred solvent for this reaction is 1,2-dichloroethane. Other solvents which may be employed, depending on the reactants or products include  
 5 toluene, acetonitrile, methylene chloride, ethyl acetate, dimethylformamide, and methyl isobutyl ketone (MIBK).

In general, depending on the nature of the reactants and the cyanide source, the rearrangement may be conducted at temperatures up to about 50°C.

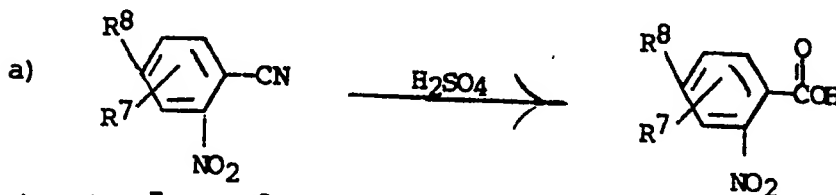
- 10 The above described substituted benzoyl chlorides can be prepared from the corresponding substituted benzoic acids according to the teaching of Reagents for Organic Synthesis, Vol. I, L.F. Fieser and M. Fieser, pp. 767-769 (1967).



wherein R<sup>7</sup> and R<sup>8</sup> are as previously defined.

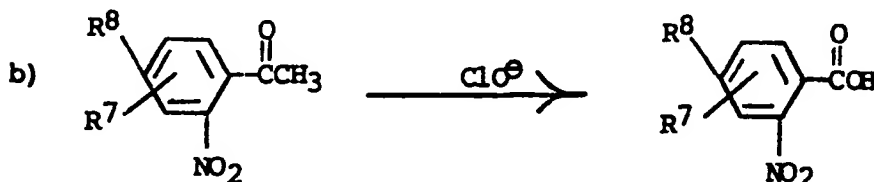
- 15 The substituted benzoic acids can be prepared by a wide variety of general methods according to the teaching of The Chemistry of Carboxylic Acids and Esters, S. Patai, editor, J. Wiley and Sons, New York, N.Y. (1969) and Survey of Organic Synthesis, C.A. Buehler and D.F. Pearson, J. Wiley and Sons, (1970).

- 20 The following are three representative examples of the methods described therein.



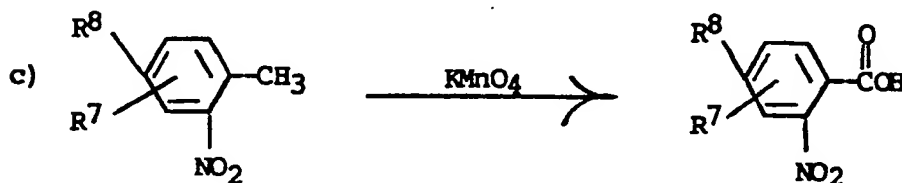
wherein R<sup>7</sup> and R<sup>8</sup> are as previously defined.

In reaction (a) the substituted benzonitrile is heated to reflux in aqueous sulfuric acid for several hours. The mixture is cooled and the reaction product is isolated by conventional techniques.



wherein  $R^7$  and  $R^8$  are as previously defined.

- 5 In reaction (b) the substituted acetophenone is heated to reflux for several hours in an aqueous hypochlorite solution. The mixture is cooled and the reaction product is isolated by conventional techniques.



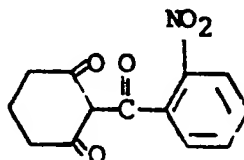
wherein  $R^7$  and  $R^8$  are as previously defined.

- 10 In reaction (c) the substituted toluene is heated to reflux in an aqueous solution of potassium permanganate for several hours. The solution is then filtered and the reaction product is isolated by conventional techniques.

The following examples teach the synthesis of representative compounds of this invention.

#### EXAMPLE 1

#### 2-(2'-Nitrobenzoyl)-1,3-cyclohexanedione

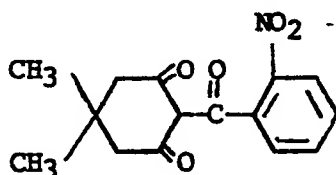


- 15 2-Nitrobenzoyl chloride (5.0 g, 27 mmol) and cyclohexanedione (3.0 g, 27 mmol) were dissolved in methylene chloride. Triethylamine (4.9

ml, 35 mmol) was added dropwise and the resulting solution stirred for one hour. The solution was washed with 2 normal hydrochloric acid (2N HCl), water, 5% potassium carbonate solution and saturated sodium chloride solution, dried over anhydrous magnesium sulfate ( $\text{MgSO}_4$ ) and concentrated under vacuum. The residue was dissolved in 20 ml acetonitrile. Triethylamine (1 equivalent) and potassium cyanide (40 mol %) were added and the solution stirred for one hour at room temperature. After dilution with ether, the solution was washed with 2N HCl and extracted with 5% potassium carbonate solution. The aqueous extract was acidified and ether was added. Filtration of the resulting mixture yielded 3.2 g of the desired compound (m.p.  $132-135^\circ\text{C}$ ) which was identified by nuclear magnetic resonance spectroscopy, infrared spectroscopy and mass spectroscopy.

#### EXAMPLE 2

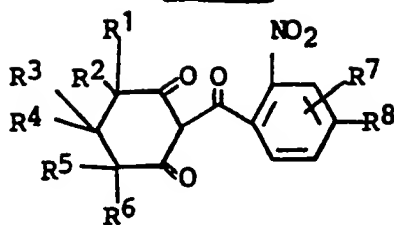
##### 2-(2'-Nitrobenzoyl)-5,5-dimethyl-1,3-cyclohexanedione



Triethylamine (3.4 ml, 25 mmol) was added dropwise to a methylene chloride solution of 2-nitrobenzoyl chloride (3.5 g, 19 mmol) and 5,5-dimethylcyclohexanedione (2.4 g, 19 mmol). After stirring for one hour at room temperature an additional 3 equivalents of triethylamine and 0.4 ml acetone cyanohydrin were added. The solution was stirred for 2.5 hours, then washed with 2N HCl and extracted with 5% potassium carbonate solution. The basic extracts were acidified with 2N HCl and extracted with ether. The ether portion was washed with saturated sodium chloride solution, dried over anhydrous magnesium sulfate and concentrated under vacuum. The residue was recrystallized from ethyl acetate yielding 2.0 g of the desired compound (m.p.  $130-133^\circ\text{C}$ ) which was identified as such by nuclear magnetic resonance spectroscopy, infrared spectroscopy and mass spectroscopy.

The following is a table of certain selected compounds that are preparable according to the procedure described hereto. Compound numbers are assigned to each compound and are used throughout the remainder of the application.

TABLE I



Comp. No.	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>	R <sup>5</sup>	R <sup>6</sup>	R <sup>7</sup>	R <sup>8</sup>	n <sub>D</sub> <sup>30</sup> or m.p.
1	CH <sub>3</sub>	H	H	H	H	H	H	H	viscous oil
2	CH <sub>3</sub>	CH <sub>3</sub>	H	H	CH <sub>3</sub>	H	H	H	viscous oil
3a)	H	H	H	H	H	H	H	H	132-135
4	CH <sub>3</sub>	CH <sub>3</sub>	H	H	H	H	H	H	viscous oil
5b)	H	H	CH <sub>3</sub>	CH <sub>3</sub>	H	H	H	H	130-133
6	CH <sub>3</sub>	H	H	H	CH <sub>3</sub>	H	H	H	viscous oil
7	CH <sub>3</sub>	CH <sub>3</sub>	H	H	H	H	H	CF <sub>3</sub>	52-61
8	H	H	H	H	H	H	H	CF <sub>3</sub>	88-94
9	H	H	CH <sub>3</sub>	CH <sub>3</sub>	H	H	H	CF <sub>3</sub>	89-97
10	CH <sub>3</sub>	CH <sub>3</sub>	H	H	H	H	3-CH <sub>3</sub>	H	119-122
11	CH <sub>3</sub>	CH <sub>3</sub>	H	H	H	H	3-Cl	H	72-79
12	CH <sub>3</sub>	CH <sub>3</sub>	H	H	H	H	H	Cl	118-121
13	CH <sub>3</sub>	CH <sub>3</sub>	H	H	H	H	5-Cl	H	118-120
14	CH <sub>3</sub>	CH <sub>3</sub>	H	H	H	H	5-F	H	130-133
15	CH <sub>3</sub>	CH <sub>3</sub>	H	H	H	H	3-CH <sub>3</sub> O	H	139-142
16	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	H	H	H	H	CF <sub>3</sub>	viscous oil
17	CH <sub>3</sub>	CH <sub>3</sub>	H	H	H	H	H	NO <sub>2</sub>	viscous oil
18	CH <sub>3</sub>	CH <sub>3</sub>	H	H	H	H	H	Br	viscous oil
19	CH <sub>3</sub>	CH <sub>3</sub>	H	H	H	CH <sub>3</sub>	5-CH <sub>3</sub>	H	viscous oil
20	CH <sub>3</sub>	CH <sub>3</sub>	H	H	H	H	5-CH <sub>3</sub>	H	viscous oil
21	H	H	H	H	H	H	H	F	123-128
22	CH <sub>3</sub>	CH <sub>3</sub>	H	H	H	H	H	F	viscous oil
23	H	H	H	H	H	H	H	Cl	viscous oil
24	CH <sub>3</sub>	CH <sub>3</sub>	H	H	H	H	H	SO <sub>2</sub> CH <sub>3</sub>	130-133
25	CH <sub>3</sub>	CH <sub>3</sub>	H	H	H	H	H	SO <sub>2</sub> -n-C <sub>3</sub> H <sub>7</sub>	viscous oil
26	H	H	H	H	H	H	H	SO <sub>2</sub> CH <sub>3</sub>	157-159
27	H	H	H	H	H	H	H	SO <sub>2</sub> -n-C <sub>3</sub> H <sub>7</sub>	120-123
28	CH <sub>3</sub>	CH <sub>3</sub>	H	H	H	H	5-F	H	165-195

TABLE I  
(continued)

Comp. No.	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>	R <sub>5</sub>	R <sub>6</sub>	R <sub>7</sub>	R <sub>8</sub>	$\eta_D^{30}$ or m.p.
29	CH <sub>3</sub>	CH <sub>3</sub>	H	H	H	H	H	SO <sub>2</sub> -C <sub>2</sub> H <sub>5</sub>	oil
30	CH <sub>3</sub>	CH <sub>3</sub>	H	H	CH <sub>3</sub>	H	H	SO <sub>2</sub> -CH <sub>3</sub>	gum
31	CH <sub>3</sub>	n-C <sub>4</sub> H <sub>9</sub>	H	H	H	H	H	H	viscous oil
32	H	H	i-C <sub>4</sub> H <sub>9</sub>	H	H	H	H	H	viscous oil
33	H	H	H	H	H	H	H	SO <sub>2</sub> -C <sub>2</sub> H <sub>5</sub>	viscous oil
34	H	H	H	H	H	H	H	CN	viscous oil
35	H	H	H	H	H	H	H	SO <sub>2</sub> N(CH <sub>3</sub> ) <sub>2</sub>	158-159
36	CH <sub>3</sub>	CH <sub>3</sub>	H	H	H	H	H	SO <sub>2</sub> N(CH <sub>3</sub> ) <sub>2</sub>	120-130
37	H	H	H	H	H	H	H	SO <sub>2</sub> N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	158-163
38	CH <sub>3</sub>	CH <sub>3</sub>	H	H	H	H	H	SO <sub>2</sub> N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	oil
39	CH <sub>3</sub>	CH <sub>3</sub>	H	H	H	H	H	SO <sub>2</sub> -N $\begin{array}{l} \text{CH}_3 \\ \text{n-C}_4\text{H}_9 \end{array}$	oil
40	H	H	CH <sub>3</sub>	CH <sub>3</sub>	H	H	H	SO <sub>2</sub> -N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	oil
41	H	H	H	H	H	H	H	SC <sub>2</sub> H <sub>5</sub>	oil
42	H	H	H	H	H	H	H	S(O)-n-C <sub>3</sub> H <sub>7</sub>	oil
43	H	H	H	H	H	H	H	S-n-C <sub>3</sub> H <sub>7</sub>	oil
44	CH <sub>3</sub>	CH <sub>3</sub>	H	H	CH <sub>3</sub>	H	H	S-n-C <sub>3</sub> H <sub>7</sub>	oil
45	CH <sub>3</sub>	CH <sub>3</sub>	H	H	H	H	H	S-n-C <sub>3</sub> H <sub>7</sub>	oil
46	CH <sub>3</sub>	CH <sub>3</sub>	H	H	CH <sub>3</sub>	H	H	S-C <sub>2</sub> H <sub>5</sub>	oil
47	CH <sub>3</sub>	CH <sub>3</sub>	H	H	H	H	H	S-C <sub>2</sub> H <sub>5</sub>	oil
48	H	H	H	H	H	H	H	S-CH <sub>3</sub>	94-97
49	CH <sub>3</sub>	CH <sub>3</sub>	H	H	CH <sub>3</sub>	H	H	CF <sub>3</sub>	oil
50	CH <sub>3</sub>	CH <sub>3</sub>	H	H	H	H	H	S-CH <sub>3</sub>	oil
51	c)	H	i-C <sub>3</sub> H <sub>7</sub>	H	H	H	H	H	145-148
52	CH <sub>3</sub>	CH <sub>3</sub>	H	H	H	H	H	5-CH <sub>3</sub> O Br	oil
53	H	H	CH <sub>3</sub>	CH <sub>3</sub>	H	H	H	Cl	oil
54	H	H	H	H	H	H	H	3-CH <sub>3</sub> O Cl	oil
55	CH <sub>3</sub>	CH <sub>3</sub>	H	H	H	H	H	3-CH <sub>3</sub> O Cl	oil
56	CH <sub>3</sub>	CH <sub>3</sub>	H	H	CH <sub>3</sub>	H	H	CH <sub>3</sub> S	oil
57	H	H	H	H	H	H	H	SO <sub>2</sub> -N $\begin{array}{l} \text{H} \\ \text{n-C}_3\text{H}_7 \end{array}$	120-125

TABLE I  
(continued)

Comp. No.	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>	R <sub>5</sub>	R <sub>6</sub>	R <sub>7</sub>	R <sub>8</sub>	$n_D^{30}$ or m.p.
58	H	H	CH <sub>3</sub>	CH <sub>3</sub>	H	H	H	CN	175-177
59	CH <sub>3</sub>	CH <sub>3</sub>	H	H	H	H	H	CN	151-153
60	CH <sub>3</sub>	CH <sub>3</sub>	H	H	CH <sub>3</sub>	H	H	CN	oil
61	c)	H	H	H	H	H	H	H	oil
62	d)	H	H	H	H	H	H	H	oil
63	H	H	CH <sub>3</sub>	H	H	H	H	Cl	110-115
64	H	H	CH <sub>3</sub>	H	H	H	H	SO <sub>2</sub> -n-C <sub>3</sub> H <sub>7</sub>	oil
65	d)	CH <sub>3</sub>	H	H	H	H	H	Cl	oil
66	H	H	H	H	H	H	H	SO <sub>2</sub> CHCl <sub>2</sub>	oil
67	CH <sub>3</sub>	CH <sub>3</sub>	H	H	H	H	H	SO <sub>2</sub> CHCl <sub>2</sub>	oil
68	H	H	H	H	H	H	c)	Br	oil
69	H	H	H	H	H	H	H	SO <sub>2</sub> CH <sub>2</sub> Cl	oil
70	CH <sub>3</sub>	CH <sub>3</sub>	H	H	H	H	H	SO <sub>2</sub> CH <sub>2</sub> Cl	wax
71	d)	CH <sub>3</sub>	H	H	H	H	H	H	oil
72	H	H	H	H	H	H	C <sub>2</sub> H <sub>5</sub> O	Cl	oil
73	CH <sub>3</sub>	CH <sub>3</sub>	H	H	CH <sub>3</sub>	H	CH <sub>3</sub> O	CF <sub>3</sub>	oil

a) Prepared in Example I.

c) = C<sub>2</sub>H<sub>5</sub>OC(O)-

b) Prepared in Example II.

d) = i-C<sub>3</sub>H<sub>7</sub>OC(O)-

#### Herbicidal Screening Tests

As previously mentioned, the herein described compounds produced in the above-described manner are phytotoxic compounds which are useful and valuable in controlling various plant species. Selected compounds of this invention were tested as herbicides in the following manner.

- 5      Pre-emergence herbicide test. On the day preceding treatment, seeds of eight different weed species are planted in loamy sand soil in individual rows using one species per row across the width of a flat. The seeds used are green foxtail (FT) (Setaria viridis), watergrass (WG) (Echinochloa crusgalli), wild oat (WO) (Avena fatua), annual morningglory

(AMG) (Ipomoea lacunosa), velvetleaf (VL) (Abutilon theophrasti), Indian mustard (MD) (Brassica juncea), curly dock (CD) (Rumex crispus), and yellow nutsedge (YNG) (Cyperus esculentus). Ample seeds are planted to give about 20 to 40 seedlings per row, after emergence, depending upon the size of the plants.

Using an analytical balance, 600 milligrams (mg) of the compound to be tested are weighed out on a piece of glassine weighing paper. The paper and compound are placed in a 60 milliliter (ml) wide-mouth clear bottle and dissolved in 45 ml of acetone or substituted solvent. Eighteen ml of this solution are transferred to a 60 ml wide-mouth clear bottle and diluted with 22 ml of a water and acetone mixture (19:1) containing enough polyoxyethylene sorbitan monolaurate emulsifier to give a final solution of 0.5% (v/v). The solution is then sprayed on a seeded flat on a linear spray table calibrated to deliver 80 gallons per acre (748 L/ha). The application rate is 4 lb/acre (4.48 Kg/ha).

After treatment, the flats are placed in the greenhouse at a temperature of 70 to 80°F and watered by sprinkling. Two weeks after treatment, the degree of injury or control is determined by comparison with untreated check plants of the same age. The injury rating from 0 to 100% is recorded for each species as percent control with 0% representing no injury and 100% representing complete control.

The results of the tests are shown in the following Table II.

TABLE II

Pre-Emergence Herbicidal Activity  
Application Rate — 4.48 kg/ha

Cmpd. No.	FT	WG	WO	AMG	VL	MD	CD	YNG
1	100	100	85	30	100	100	90	90
2	100	100	100	50	100	100	95	95
3	100	100	85	25	100	100	100	95
4	100	100	100	20	100	85	95	90
5	100	100	45	25	100	100	90	90
6	100	100	95	40	100	100	85	90
9	100	100	90	90	100	100	80	90
10	100	90	20	10	100	70	100	90
11	90	100	50	230	100	100	90	90
12	100	100	95	80	100	100	90	90
13	40	75	0	10	80	100	100	90
14	50	0	0	0	100	80	70	90
15	65	95	20	15	100	80	90	85
17	100	100	60	30	100	100	90	35
18	100	100	100	100	100	100	100	95
19	100	100	0	50	100	100	100	95
20	75	100	0	25	100	90	65	90
21	100	100	100	80	100	100	90	95
22	100	100	100	80	100	100	95	95
23	100	100	98	95	100	100	100	95
25	100	100	80	100	100	100	80	-
26	100	100	75	100	100	100	80	-
27	90	100	50	100	100	100	100	90
28	75	50	50	0	100	100	90	65
30	100	100	85	100	100	100	95	90
31	85	75	0	25	100	25	0	35
32	83	85	35	20	95	100	75	50
36	100	100	50	100	100	100	100	75
37	20	75	0	20	100	95	100	75
38	85	95	40	60	100	100	75	85
39	85	95	45	75	100	95	70	90
51	60	60	35	0	25	0	0	30
52	75	75	0	50	90	75	40	0
65	100	100	80	100	100	100	-	80

A blank (-) indicates that the weed was not tested.



Post-Emergence Herbicide Test: This test is conducted in an identical manner to the testing procedure for the pre-emergence herbicide test, except the seeds of the eight different weed species are planted 10-12 days before treatment. Also, watering of the treated flats is confined  
5 to the soil surface and not to the foliage of the sprouted plants.

The results of the post-emergence herbicide test are reported in Table III.

TABLE III

Post-Emergence Herbicidal Activity  
Application Rate — 4.48 kg/ha

Ompd. No.	FT	WG	WO	AMG	VL	MD	CD	YNG
1	95	75	85	70	100	90	85	40
2	45	70	95	75	100	90	100	65
3	100	80	100	90	-	100	100	80
4	100	80	100	100	-	100	85	75
5	90	70	45	60	95	70	60	80
6	95	75	80	70	100	90	90	65
9	100	90	90	100	100	100	95	85
10	45	75	10	15	100	100	20	75
11	100	70	60	75	100	100	100	45
12	100	75	100	100	100	100	90	90
13	30	55	0	30	60	60	15	60
14	20	65	0	40	70	60	40	25
15	20	75	30	20	100	70	60	40
17	85	80	50	65	95	95	100	60
18	100	95	100	100	100	100	100	75
19	20	95	30	100	100	35	30	70
20	30	80	15	100	100	45	20	70
21	100	80	100	55	100	90	100	80
22	100	80	100	60	100	95	95	95
23	100	90	90	100	100	100	85	70
25	70	75	50	85	90	85	60	75
26	100	85	85	95	95	95	90	60
27	90	90	60	100	100	100	100	-
28	15	45	20	50	75	80	15	30
30	100	100	80	85	85	85	100	-
31	80	90	100	100	100	100	100	60
32	75	85	85	75	75	90	95	50
36	35	50	35	70	50	50	35	60
37	60	75	15	70	70	90	90	40
38	95	90	65	70	90	90	100	50
39	95	85	30	50	70	80	100	50
51	60	75	60	35	30	60	40	60
52	60	75	25	100	100	100	100	75
65	70	50	70	90	80	85	-	80

A blank (-) indicates the weed was not tested.

Pre-Emergence Multi-Weed Herbicide Test

Several compounds were evaluated at an application rate of 2, 1, 1/2 or 1/4 lb/acre (2.24, 1.12, 0.56 or 0.28 kg/ha) for pre-emergence activity against a larger number of weed species.

The process was generally similar to the pre-emergence herbicide test described above except that only 300, 150, 75 or 37.5 milligrams of test compound were weighed out and the application rate was 40 gallons per acre.

Redroot pigweed (PW) and curly dock (CD) were eliminated in this test and the following weed species were added:

10	<u>Grasses:</u>	downy brome	<u>Bromus tectorum</u>	(DB)
		annual ryegrass	<u>Lolium multiflorum</u>	(ARG)
		shattercane	<u>Sorghum bicolor</u>	(SBC)
		hemp sesbania	<u>Sesbania exaltata</u>	(SESB)
		sickepod	<u>Cassia obtusifolia</u>	(SP)
15		cocklebur	<u>Xanthium sp.</u>	(CB)
		broadleaf signalgrass	<u>Brachiaria platyphylla</u>	(BSG)

The results of the test are shown in Tables IV, V and VI.

TABLE IV  
Pre-Emergence Multi-weed Herbicide Test

Application Rate - 2.24 kg/ha

Compd. No.	DB	FT	ARG	WG	SHC	WO	BSG	AMG	SESB	VL	SP	MD	YNG	CB
7	100	100	100	100	100	100	100	100	100	100	100	100	95	100
8	100	100	100	100	100	100	100	100	100	100	100	100	95	-
16a	70	100	65	100	100	60	98	55	100	100	90	100	90	-
24	100	100	100	100	100	100	100	100	100	100	100	100	100	-
29	100	100	100	100	100	100	100	100	100	100	30	100	95	80
33	75	15	60	90	90	20	95	100	100	100	60	100	95	100
53	100	100	100	100	100	90	100	100	100	100	100	100	95	100
57	100	100	25	100	100	30	25	100	100	100	100	100	95	100
64a	-	0	0	95	35	0	15	50	75	75	25	-	75	40
66a	-	0	15	15	50	20	50	100	100	75	0	-	90	100
67a	-	0	0	100	100	0	25	95	75	50	25	-	30	75
69a	-	30	0	100	100	0	70	100	100	100	35	-	95	100
70a	-	100	10	100	100	25	65	100	100	100	0	-	95	100

(-) = Not tested.

(a) = Tested at 0.28 kg/ha.

TABLE V  
Pre-Emergence Multi-weed Herbicide Test

Application Rate - 1.12 kg/ha

Compd. No.	DB	FT	ARG	WG	SHC	WO	BSG	AMG	SESB	VL	SP	MD	YNG	CB
34	90	85	30	95	-	45	98	75	100	100	40	100	50	-
35	100	85	70	100	-	90	100	100	100	100	40	100	75	-
40	100	100	20	100	-	70	100	98	98	100	20	100	50	-
41	100	100	80	100	-	60	100	100	100	100	25	100	95	-
42	50	60	40	85	-	30	100	100	100	100	100	100	90	-
43	90	95	60	100	-	30	98	100	98	100	45	100	95	-
44	60	100	20	100	-	60	100	100	90	100	20	100	80	-
45	95	100	35	100	-	60	90	100	100	100	0	100	90	-
46	100	100	90	100	-	95	100	100	100	100	40	100	95	-
47	100	100	100	100	-	98	100	100	98	100	30	100	95	-
48	100	100	100	100	-	100	100	100	100	100	90	100	100	-
49	100	100	100	100	-	100	100	100	100	100	90	100	-	-
50	100	100	100	100	100	85	100	100	100	100	90	100	98	-
54	100	100	85	100	100	15	100	25	100	100	65	100	95	100
55	85	100	35	100	98	15	100	15	100	100	65	100	95	-
56	100	100	100	100	100	100	100	100	100	100	100	100	100	100
58	98	100	40	95	40	20	95	100	100	100	85	100	100	95
59	100	100	100	100	100	90	100	100	100	100	100	100	85	80
60	100	100	100	100	100	100	100	100	100	100	75	100	85	80

(-) = Not tested.

TABLE VI

Pre-Emergence Multi-weed Herbicide Test

Application Rate - 0.56 kg/ha

Ompd. No.	DB	FT	ARG	WG	SHC	WO	BSG	AMG	SESB	VL	SP	MD	YNG	CB
61	-	100	65	100	65	20	80	20	40	80	10	-	20	0
62	-	50	35	70	50	0	0	0	25	50	0	-	0	0
63	100	100	100	100	100	95	100	90	95	100	75	100	100	85
68	-	0	20	0	0	0	0	60	100	100	90	-	75	75
71	-	50	40	50	75	40	35	75	50	70	0	-	75	75
72	-	35	60	100	85	50	100	25	65	100	35	-	100	35
73	-	90	70	100	95	25	0	70	100	100	0	-	50	25

(-) = Not tested.

Post-Emergence Multi-Weed Herbicide Test: This test is conducted in an identical manner to the testing procedure for the post-emergence herbicide test, except the seeds of the eight weed species used in the pre-emergence multi-weed herbicide test were used and the seeds  
 5 were planted 10-12 days before treatment. Also, watering of the treated flats is confined to the soil surface and not to the foliage of the sprouted plants.

The results of the post-emergence multi-weed herbicide test are reported in Tables VII, VIII and IX.

TABLE VII

Post-Emergence Multi-Weed Herbicidal Activity  
Application Rate — 2.24 kg/ha

Ompd.	No.	DB	FT	ARG	WG	SHC	WO	BSG	AMG	SESB	VL	SP	MD	YNG	CB
	7	100	100	100	100	80	90	10	95	100	100	55	100	45	100
	16a	100	85	35	100	100	100	100	100	100	100	100	100	85	70
	24	100	100	100	100	100	100	100	100	100	100	100	100	100	-
	29	100	100	60	100	90	100	100	100	100	100	100	100	100	-
	33	90	98	85	100	100	80	100	100	100	100	90	100	90	100
	53	100	100	60	100	100	100	100	100	100	100	100	100	100	-
	57	25	40	10	100	10	0	10	100	95	100	35	100	-	100
	64a	-	0	0	90	0	0	85	40	100	80	50	-	35	100
	66a	-	0	0	65	0	0	70	75	80	75	0	-	25	75
	67a	-	0	0	75	35	0	40	70	80	60	0	-	0	100
	69a	-	0	0	80	35	0	100	90	100	100	40	-	35	100
	70a	-	100	0	100	70	90	90	100	100	100	30	-	25	100

(-) = Not tested.

(a) = Tested at 0.28 kg/ha.

TABLE VIII

Post-Emergence Multi-weed Herbicide Test

Application Rate - 1.12 kg/ha

Ompd.	No.	DB	FT	ARG	WG	SHC	WO	BSG	AMG	SESB	VL	SP	MD	YNG	CB
	34	90	85	30	95	-	45	98	75	100	100	40	100	50	-
	35	100	85	70	100	-	90	100	100	100	100	40	100	75	-
	40	75	100	5	100	-	50	75	100	100	100	40	100	30	-
	41-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	42	40	100	35	100	-	50	80	100	100	100	80	100	70	-
	43	60	70	20	100	-	55	60	100	100	100	95	100	70	-
	44	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	45	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	46	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	47	90	100	35	100	-	75	90	100	100	100	25	100	45	-
	48	80	100	60	100	-	60	80	100	100	100	85	100	60	-
	49	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	50	90	80	60	95	80	90	100	100	100	100	65	100	80	-
	54	35	50	30	100	30	15	90	100	100	100	100	100	95	-
	55	100	100	20	100	90	20	100	90	100	100	100	100	-	-
	56	75	90	75	95	90	25	100	100	100	100	90	100	90	100
	58	70	100	40	100	95	30	95	100	95	100	95	100	95	85
	59	90	100	95	100	100	50	100	100	100	100	95	100	100	95
	60	95	100	100	100	100	75	95	100	100	100	95	100	100	100

(-) = Not tested.

TABLE IX  
Post-Emergence Multi-weed Herbicide Test  
 Application Rate - 0.56 kg/ha

Compd.	No.	DB	FT	ARG	WG	SHC	WO	BSG	AMG	SESB	VL	SP	MD	YNG	CB
	61	-	40	0	50	35	0	40	75	95	100	0	-	25	50
	62	-	35	0	20	0	0	20	35	60	100	0	-	0	100
	63	100	100	85	98	85	100	100	100	100	100	100	85	85	95
	68	-	30	40	85	0	25	60	80	95	100	95	-	0	80
	71	-	50	0	80	65	0	75	100	80	100	50	-	25	100
	72	-	90	70	80	50	50	75	85	100	100	90	-	100	100
	73	-	100	15	100	75	75	85	100	100	90	60	-	80	100

(-) = Not tested.

- The compounds of the present invention are useful as herbicides and can be applied in a variety of ways at various concentrations. In practice, the compounds herein defined are formulated into herbicidal compositions, by admixture, in herbicidally effective amounts, with the
- 5    adjuvants and carriers normally employed for facilitating the dispersion of active ingredients for agricultural applications, recognizing the fact that the formulation and mode of application of a toxicant may affect the activity of the materials in a given application. Thus, these active herbicidal compounds may be formulated as granules of relatively large
- 10   particle size, as wettable powders, as emulsifiable concentrates, as powdery dusts, as solutions or as any of several other known types of formulations, depending upon the desired mode of application. Preferred formulations for pre-emergence herbicidal applications are wettable powders, emulsifiable concentrates and granules. These formulations may con-
- 15   tain as little as about 0.5% to as much as about 95% or more by weight of active ingredient. A herbicidally effective amount depends upon the nature of the seeds or plants to be controlled and the rate of application varies from about 0.05 to approximately 25 pounds per acre, preferably from about 0.1 to about 10 pounds per acre.
- 20       Wettable powders are in the form of finely divided particles which disperse readily in water or other dispersants. The wettable powder is ultimately applied to the soil either as a dry dust or as a dispersion in water or other liquid. Typical carriers for wettable powders include

fuller's earth, kaolin clays, silicas and other readily wet organic or inorganic diluents. Wettable powders normally are prepared to contain about 5% to about 95% of the active ingredient and usually also contain a small amount of wetting, dispersing, or emulsifying agent to facilitate wetting and dispersion.

Emulsifiable concentrates are homogeneous liquid compositions which are dispersible in water or other dispersant, and may consist entirely of the active compound with a liquid or solid emulsifying agent, or may also contain a liquid carrier, such as xylene, heavy aromatic naphthal, isophorone and other non-volatile organic solvents. For herbicidal application, these concentrates are dispersed in water or other liquid carrier and normally applied as a spray to the area to be treated. The percentage by weight of the essential active ingredient may vary according to the manner in which the composition is to be applied, but in general comprises about 0.5% to 95% of active ingredient by weight of the herbicidal composition.

Granular formulations wherein the toxicant is carried on relatively coarse particles, are usually applied without dilution to the area in which suppression of vegetation is desired. Typical carriers for granular formulations include sand, fuller's earth, bentonite clays, vermiculite, perlite and other organic or inorganic materials which absorb or which may be coated with the toxicant. Granular formulations normally are prepared to contain about 5% to about 25% of active ingredients which may include surface-active agents such heavy aromatic naphthas, kerosene or other petroleum fractions, or vegetable oils; and/or stickers such as destrins, glue or synthetic resins.

Typical wetting, dispersing or emulsifying agents used in agricultural formulations include, for example, the alkyl and alkylaryl sulfonates and sulfates and their sodium salts; polyhydric alcohols; and other types of surface-active agents, many of which are available in commerce. The surface-active agent, when used, normally comprises from 0.1% to 15% by weight of the herbicidal composition.



Dusts, which are free-flowing admixtures of the active ingredient with finely divided solids such as talc, clays, flours and other organic and inorganic solids which act as dispersants and carriers for the toxicant, are useful formulations for soil-incorporating application.

5           Pastes, which are homogeneous suspensions of a finely divided solid toxicant in a liquid carrier such as water or oil, are employed for specific purposes. These formulations normally contain about 5% to about 95% of active ingredient by weight, and may also contain small amounts of a wetting, dispersing or emulsifying agent to facilitate dispersion. For  
10 application, the pastes are normally diluted and applied as a spray to the area to be affected.

Other useful formulations for herbicidal applications include simple solutions of the active ingredient in a dispersant in which it is completely soluble at the desired concentration, such as acetone, alkyl-  
15 ated naphthalenes, xylene and other organic solvents. Pressurized sprays, typically aerosols, wherein the active ingredient is dispersed in finely-divided form as a result of vaporization of a low boiling dispersant solvent carrier, such as the Freons, may also be used.

The phytotoxic compositions of this invention are applied to the  
20 plants in the conventional manner. Thus, the dust and liquid compositions can be applied to the plant by the use of power-dusters, boom and hand sprayers and spray dusters. The compositions can also be applied from airplanes as a dust or a spray because they are effective in very low dosages. In order to modify or control growth of germinating seeds or  
25 emerging seedlings, as a typical example, the dust and liquid compositions are applied to the soil according to conventional methods and are distributed in the soil to a depth of at least 1/2 inch below the soil surface. It is not necessary that the phytotoxic compositions be admixed with the soil particles since these compositions can also be applied merely by  
30 spraying or sprinkling the surface of the soil. The phytotoxic compositions of this invention can also be applied by addition to irrigation water supplied to the field to be treated. This method of application permits the penetration of the compositions into the soil as the water is absorbed therein. Dust compositions, granular compositions or liquid

formulations applied to the surface of the soil can be distributed below the surface of the soil by conventional means such as disking, dragging or mixing operations.

### EMULSIFIABLE CONCENTRATE FORMULATIONS

<u>General Formula with Ranges</u>		<u>Specific Formula</u>	
Herbicidal compound	5-55	herbicidal compound	54
surfactant(s)	5-25	proprietary blend of oil-soluble sulfonates and polyoxyethylene ethers	10
solvent(s)	20-90	polar solvent	27
	<u>100%</u>	petroleum hydrocarbon	9
			<u>100%</u>

### WETTABLE POWDER FORMULATIONS

herbicidal compound	3-90	herbicidal compound	80
wetting agent	0.5-2	sodium dialkyl naphthalene sulfonate	0.5
dispersing agent	1-8	sodium lignosulfonate	7
diluent(s)	8.5-87	attapulgitic clay	12.5
	<u>100%</u>		<u>100%</u>

### EXTRUDED GRANULAR FORMULATIONS

herbicidal compound	1-20	herbicidal compound	10
binding agent	0-10	lignin sulfonate	5
diluent(s)	70-99	calcium carbonate	85
	<u>100%</u>		<u>100%</u>

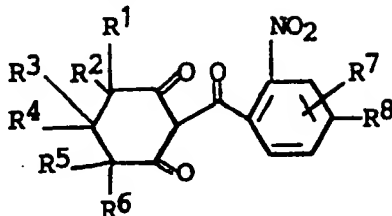
### FLOWABLE FORMULATIONS

herbicidal compound	20-70	herbicidal compound	45
surfactant(s)	1-10	polyoxyethylene ether	5
suspending agent(s)	0.05-1	attagel	0.05
antifreeze agent	1-10	propylene glycol	10
antimicrobial agent	1-10	BIT	0.03
antifoam agent	0.1-1	silicone defoamer	0.02
solvent	7.95-77.85	water	39.9
	<u>100%</u>		<u>100%</u>

The phytotoxic compositions of this invention can also contain other additaments, for example, fertilizers and other herbicides, pesticides and the like, used as adjuvant or in combination with any of the above-described adjuvants. Other phytotoxic compounds useful in combination with the above-described compounds include, for example, anilides such as 2-benzothiazole-2-yloxy-N-methyl acetanilide, 2-chloro-2',6'-dimethyl-N-(n-propylethyl) acetanilide, 2-chloro-2',6'-diethyl-N-(butoxymethyl) acetanilide; 2,4-dichlorophenoxyacetic acids, 2,4,5-trichlorophenoxyacetic acid, 2-methyl-4-chlorophenoxyacetic acid and the salts, esters and amides thereof; triazine derivatives, such as 2,4-bis(3-methoxypropylamino)-6-methylthio-s-triazine, 2-chloro-4-ethylamino-6-isopropylamino-s-triazine, and 2-ethylamino-4-isopropylamino-6-methyl-mercapto-s-triazine; urea derivatives, such as 3-(3,5-dichlorophenyl)-1,1-dimethylurea and 3-(p-chlorophenyl)-1,1-dimethylurea; and acetamides such as N,N-diallyl-  
 15  $\alpha$ -chloroacetamide, and the like; benzoic acids such as 3-amino-2,5-dichlorobenzoic acid; thiocarbamates such as S-(1,1-dimethylbenzyl)-piperidine-1-carbothioate, 3-(4-chlorophenyl)-methyl diethylcarbothioate, ethyl-1-hexahydro-1,4-azepine-1-carbothioate, S-ethyl-hexahydro-1H-azepine-1-carbothioate, S-propyl N,N-dipropylthiocarbamate, S-ethyl N,N-dipropylthiocarbamate, S-ethyl cyclohexylethylthiocarbamate and the like; anilines such as 4-(methylsulfonyl)-2,6-dinitro-N,N-substituted aniline, 4-trifluoromethyl-2,6-dinitro-N,N-dipn-propyl aniline, 4-trifluoromethyl-2,6-dinitro-N-ethyl-N-butyl aniline, 2-[4-(2,4-dichlorophenoxy)phenoxy]propanoic acid, 2-[1-(ethoxyimino)butyl]-5-[2-ethylthio)propyl]-3-hydroxy-  
 20 2-cyclohexene-1-one, (+)-butyl-2[4-[(5-trifluoromethyl)-2-pyridinyl)oxy]phenoxy]propanate, sodium 5-[2-chloro-4-(trifluoromethyl)phenoxy]-2-nitrobenzoate, 3-isopropyl-1H-2,1,3-benzothiadiazine-4(3H)-one-2,2-dioxide, and 4-amino-6-tert-butyl-3(methylthio)-as-triazin-5(4H)-one or 4-amino-6-(1,1-dimethylethyl)-3-(methylthio)-1,2,4-triazin-5(4H)-one and S-(O,O-diisopropyl)-benzene sulfonamide. Fertilizers useful in combination with the active ingredients include, for example, ammonium nitrate, urea and superphosphate. Other useful additaments include materials in which plant organisms take root and grow such as compost, manure, humus, sand, and the like.

WHAT IS CLAIMED IS:

1. A compound of the formula



wherein

$R^1$  is hydrogen or  $C_1-C_4$  alkyl;

$R^2$  is hydrogen,  $C_1-C_4$  alkyl or  $R^a-O-C(=O)-$  wherein  $R^a$  is  $C_1-C_4$

5 alkyl; or

$R^1$  and  $R^2$  together are alkylene having 3 to 6 carbon atoms;

$R^3$  is hydrogen or  $C_1-C_4$  alkyl;

$R^4$  is hydrogen or  $C_1-C_4$  alkyl;

$R^5$  is hydrogen or  $C_1-C_4$  alkyl;

10  $R^6$  is hydrogen or  $C_1-C_4$  alkyl; and

$R^7$  and  $R^8$  independently are (1) hydrogen; (2) halogen; (3)  $C_1-C_4$  alkyl; (4)  $C_1-C_4$  alkoxy; (5)  $OCF_3$ ; (6) cyano; (7) nitro; (8)  $C_1-C_4$  haloalkyl; (9)  $R^bSO_n-$  wherein  $n$  is the integer 0, 1 or 2; and  $R^b$  is (a)  $C_1-C_4$  alkyl; (b)  $C_1-C_4$  alkyl substituted with halogen or cyano; (c) phenyl; or  
15 (d) benzyl; (10)  $-NRCR^d$  wherein  $R^c$  and  $R^d$  independently are hydrogen or  $C_1-C_4$  alkyl; (11)  $REC(O)-$  wherein  $R^e$  is  $C_1-C_4$  alkyl or  $C_1-C_4$  alkoxy; or (12)  $SO_2NRCR^d$  wherein  $R^c$  and  $R^d$  are as defined, with the proviso that  $R^7$  is not attached to the 6-position.

2. The compounds of Claim 1 wherein  $R^1$  is hydrogen or methyl;  
20  $R^2$  is hydrogen or methyl;  $R^3$  is hydrogen or methyl;  $R^4$  is hydrogen or methyl;  $R^5$  is hydrogen or methyl;  $R^6$  is hydrogen or methyl;  $R^7$  and  $R^8$  independently are (1) hydrogen; (2) halogen; (3)  $C_1-C_4$  alkyl; (4)  $C_1-C_4$  alkoxy; (5)  $OCF_3$ ; (6) cyano; (7) nitro; (8)  $C_1-C_4$  haloalkyl; (9)  $R^bSO_n-$  wherein  $n$  is the integer 0, 1 or 2; and  $R^b$  is (a)  $C_1-C_4$  alkyl; (b)  $C_1-C_4$   
25 alkyl substituted with halogen or cyano; (c) phenyl; or (d) benzyl; (10)  $-NRCR^d$  wherein  $R^c$  and  $R^d$  independently are hydrogen or  $C_1-C_4$  alkyl; (11)  $REC(O)-$  wherein  $R^e$  is  $C_1-C_4$  alkyl or  $C_1-C_4$  alkoxy; or (12)  $SO_2NRCR^d$  wherein  $R^c$  and  $R^d$  are as defined.

3. The compound of Claim 2 wherein  $R^7$  and  $R^8$  are independently are hydrogen; chlorine; fluorine; bromine; methyl; methoxy;  $OCF_3$ ; cyano; nitro; trifluoromethyl;  $R^bSO_n$ - wherein  $n$  is the integer 2 and  $R^b$  is methyl, chloromethyl, trifluoromethyl, cyanomethyl, ethyl, or  $n$ -propyl;  
5  $-NRC^dR^d$  wherein  $R^c$  and  $R^d$  independently are hydrogen or  $C_1$ - $C_4$  alkyl;  
 $R^eC(O)-$  where  $R^e$  is  $C_1$ - $C_4$  alkyl or  $C_1$ - $C_4$  alkoxy or  $SO_2NRC^dR^d$  wherein  $R^c$  and  $R^d$  are as defined and  $R^7$  is in the 3-position.

4. The compound of Claim 2 wherein  $R^7$  is hydrogen and  $R^8$  is hydrogen, chlorine, bromine, fluorine,  $CF_3$  or  $R^bSO_2$  wherein  $R^b$  is  $C_1$ - $C_4$   
10 alkyl or  $C_1$ - $C_4$  haloalkyl.

5. The compound of Claim 2 wherein  $R^1$  is methyl;  $R^2$  is methyl;  $R^3$  is hydrogen;  $R^4$  is hydrogen;  $R^5$  is hydrogen;  $R^6$  is hydrogen;  $R^7$  is hydrogen; and  $R^8$  is hydrogen.

6. The compound of Claim 2 wherein  $R^1$  is methyl;  $R^2$  is methyl;  
15  $R^3$  is hydrogen;  $R^4$  is hydrogen;  $R^5$  is methyl;  $R^6$  is hydrogen;  $R^7$  is hydrogen; and  $R^8$  is hydrogen.

7. The compound of Claim 2 wherein  $R^1$  is methyl;  $R^2$  is methyl;  $R^3$  is hydrogen;  $R^4$  is hydrogen;  $R^5$  is hydrogen;  $R^6$  is hydrogen;  $R^7$  is hydrogen; and  $R^8$  is trifluoromethyl.

20 8. The compound of Claim 2 wherein  $R^1$  is hydrogen;  $R^2$  is hydrogen;  $R^3$  is hydrogen;  $R^4$  is hydrogen;  $R^5$  is hydrogen;  $R^6$  is hydrogen;  $R^7$  is hydrogen; and  $R^8$  is trifluoromethyl.

9. The compound of Claim 2 wherein  $R^1$  is methyl;  $R^2$  is methyl;  $R^3$  is hydrogen;  $R^4$  is hydrogen;  $R^5$  is hydrogen;  $R^6$  is hydrogen;  $R^7$  is  
25 hydrogen; and  $R^8$  is chlorine.

10. The compound of Claim 2 wherein  $R^1$  is methyl;  $R^2$  is methyl;  $R^3$  is hydrogen;  $R^4$  is hydrogen;  $R^5$  is hydrogen;  $R^6$  is hydrogen;  $R^7$  is hydrogen; and  $R^8$  is fluorine.

11. The compound of Claim 2 wherein  $R^1$  is hydrogen;  $R^2$  is hydrogen;  $R^3$  is hydrogen;  $R^4$  is hydrogen;  $R^5$  is hydrogen;  $R^6$  is hydrogen;  $R^7$  is hydrogen; and  $R^8$  is chlorine.

12. The compound of Claim 2 wherein  $R^1$  is methyl;  $R^2$  is methyl;  
5  $R^3$  is hydrogen;  $R^4$  is hydrogen;  $R^5$  is hydrogen;  $R^6$  is hydrogen;  $R^7$  is hydrogen; and  $R^8$  is  $\text{CH}_3\text{SO}_2^-$ .

13. The compound of Claim 2 wherein  $R^1$  is hydrogen;  $R^2$  is hydrogen;  $R^3$  is hydrogen;  $R^4$  is hydrogen;  $R^5$  is hydrogen;  $R^6$  is hydrogen;  $R^7$  is hydrogen; and  $R^8$  is  $n\text{-C}_3\text{H}_7\text{SO}_2$ .

10 14. The compound of Claim 2 wherein  $R^1$  is hydrogen;  $R^2$  is hydrogen;  $R^3$  is hydrogen;  $R^4$  is hydrogen;  $R^5$  is hydrogen;  $R^6$  is hydrogen;  $R^7$  is hydrogen; and  $R^8$  is  $\text{CH}_3\text{SO}_2$ .

15 15. The compound of Claim 2 wherein  $R^1$  is hydrogen;  $R^2$  is hydrogen;  $R^3$  is hydrogen;  $R^4$  is hydrogen;  $R^5$  is hydrogen;  $R^6$  is hydrogen; 15  $R^7$  is hydrogen; and  $R^8$  is  $\text{C}_2\text{H}_5\text{SO}_2$ .

16. The compounds of Claim 2 wherein  $R^7$  is hydrogen.

17. The compounds of Claim 3 wherein  $R^7$  is hydrogen.

18. The compound of Claim 2 wherein  $R^1$  is hydrogen;  $R^2$  is hydrogen;  $R^3$  is hydrogen;  $R^4$  is hydrogen;  $R^5$  is hydrogen;  $R^6$  is hydrogen;  
20  $R^7$  is hydrogen; and  $R^8$  is cyano.

19. The compound of Claim 1 wherein  $R^1$  and  $R^2$  are hydrogen or both methyl.

20. The compound of Claim 19 wherein  $R^8$  is  $-\text{SO}_2\text{CH}_3$ .

21. The compound of Claim 19 wherein  $R^8$  is  $-\text{SO}_2\text{CH}_2\text{Cl}$ .

25 22. The compound of Claim 1 wherein  $R^8$  is  $\text{CF}_3$ .

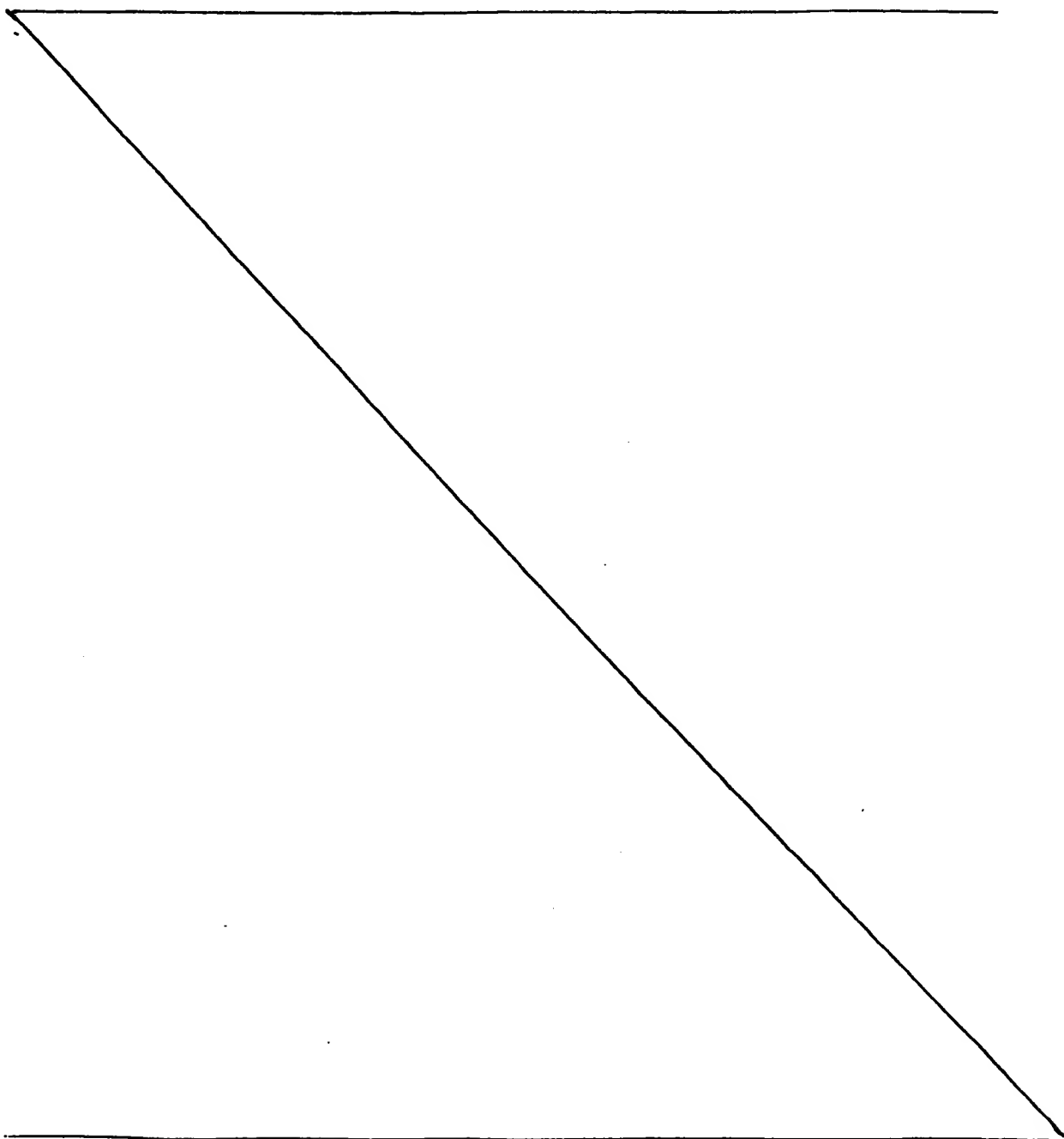
23. The compound of Claim 1 wherein  $R^8$  is  $-\text{SO}_2\text{CH}_3$ .
24. The compound of Claim 1 wherein  $R^8$  is chlorine.
25. The compound of Claim 1 wherein  $R^8$  is  $-\text{SO}_2\text{CH}_2\text{Cl}$ .
26. The compound of Claim 1 wherein  $R^8$  is  $-\text{SO}_2\text{-n-C}_3\text{H}_7$ .
- 5        27. The method of controlling undesirable vegetation comprising applying to the area where control is desired, an herbicidally effective amount of a compound described in Claims 1-26.
28. An herbicidal composition comprising an herbicidally active 2-(2-nitrobenzoyl)-1,3-cyclohexanedione and an inert carrier therefor.
- 10       29. The herbicidal composition of Claim 28 wherein the 2-(2-nitrobenzoyl)-1,3-cyclohexanedione is a compound of Claims 1-26.
30. The method of controlling undesirable vegetation comprising applying to the area where control is desired, an herbicidal composition comprising an herbicidally active 2-(2-nitrobenzoyl)-1,3-cyclohexanedione and an inert carrier therefor.
- 15       31. The method of Claim 30 wherein the 2-(2-nitrobenzoyl)-1,3-cyclohexanedione has a  $\text{C}_1\text{-C}_4$  alkylsulfonyl or  $\text{C}_1\text{-C}_4$  haloalkylsulfonyl substitution on the phenyl ring.
32. The method of Claim 31 wherein said alkylsulfonyl or halo-
- 20       alkylsulfonyl substitution is at the 4-position of the phenyl ring.
33. The herbicidal composition of Claim 28 wherein the 2-(2-nitrobenzoyl)-1,3-cyclohexanedione has a  $\text{C}_1\text{-C}_4$  alkylsulfonyl or  $\text{C}_1\text{-C}_4$  haloalkylsulfonyl substitution on the phenyl ring.
34. The herbicidal composition of Claim 32 wherein said alkyl-
- 25       sulfonyl or haloalkylsulfonyl substitution is at the 4-position of the phenyl ring.

35. The method of Claim 30 wherein the 2-(2-nitrobenzoyl)-1,3-cyclohexanedione has a  $C_1-C_4$  haloalkyl substitution on the phenyl ring.

36. The method of Claim 30 wherein said haloalkyl substitution  
5 is at the 4-position on the phenyl ring.

37. The herbicidal composition of Claim 28 wherein the 2-(2-nitrobenzoyl)-1,3-cyclohexanedione has a  $C_1-C_4$  haloalkyl substitution on the phenyl ring.

0





38. The herbicidal composition of Claim 37 wherein said haloalkyl substitution is at the 4-position of the phenyl ring.

39. The herbicidal composition of Claim 37 wherein said haloalkyl is  $\text{CF}_3$ .

5 40. The method of Claim 35 wherein said haloalkyl is  $\text{CF}_3$ .

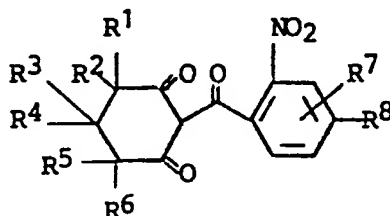
41. The method of Claim 27 wherein  $\text{R}^1$  and  $\text{R}^2$  are hydrogen or both methyl.

42. The method of Claim 41 wherein  $\text{R}^8$  is  $-\text{SO}_2\text{CH}_3$ ,  $-\text{SO}_2\text{CH}_2\text{Cl}$ ,  $\text{CF}_3$ ,  $-\text{SO}_2\text{CH}_3$ , chlorine,  $-\text{SO}_2\text{CH}_2\text{Cl}$  or  $-\text{SO}_2\text{-n-C}_3\text{H}_7$ .

10 43. The composition of matter of Claim 28 wherein  $\text{R}^1$  and  $\text{R}^2$  are hydrogen or both methyl.

44. The composition of matter of Claim 43 wherein  $\text{R}^8$  is  $-\text{SO}_2\text{CH}_3$ ,  $-\text{SO}_2\text{CH}_2\text{Cl}$ ,  $\text{CF}_3$ ,  $-\text{SO}_2\text{CH}_3$ , chlorine,  $-\text{SO}_2\text{CH}_2\text{Cl}$  or  $-\text{SO}_2\text{-n-C}_3\text{H}_7$ .

45. A process for preparing a compound of the formula



15 wherein

$\text{R}^1$  is hydrogen or  $\text{C}_1\text{-C}_4$  alkyl;

$\text{R}^2$  is hydrogen,  $\text{C}_1\text{-C}_4$  alkyl or  $\text{R}^a\text{-O-C(=O)-}$  wherein  $\text{R}^a$  is  $\text{C}_1\text{-C}_4$  alkyl; or

20  $\text{R}^1$  and  $\text{R}^2$  together are alkylene having 3 to 6 carbon atoms;

$\text{R}^3$  is hydrogen or  $\text{C}_1\text{-C}_4$  alkyl;

$\text{R}^4$  is hydrogen or  $\text{C}_1\text{-C}_4$  alkyl;

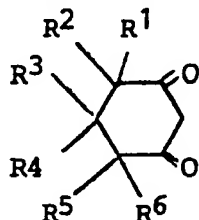
$\text{R}^5$  is hydrogen or  $\text{C}_1\text{-C}_4$  alkyl;

$\text{R}^6$  is hydrogen or  $\text{C}_1\text{-C}_4$  alkyl; and

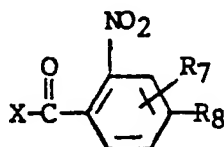
0186118

$R^7$  and  $R^8$  independently are (1) hydrogen; (2) halogen; (3)  $C_1$ - $C_4$  alkyl; (4)  $C_1$ - $C_4$  alkoxy; (5)  $OCF_3$ ; (6) cyano; (7) nitro; (8)  $C_1$ - $C_4$  haloalkyl; (9)  $R^bSO_n-$  wherein  $n$  is the integer 0, 1 or 2; and  $R^b$  is (a)  $C_1$ - $C_4$  alkyl; (b)  $C_1$ - $C_4$  alkyl substituted with halogen or cyano; (c) phenyl; or (d) benzyl; (10)  $-NRC^dR^d$  wherein  $R^c$  and  $R^d$  independently are hydrogen or  $C_1$ - $C_4$  alkyl; (11)  $REC(O)-$  wherein  $R^e$  is  $C_1$ - $C_4$  alkyl or  $C_1$ - $C_4$  alkoxy; or (12)  $SO_2NRC^dR^d$  wherein  $R^c$  and  $R^d$  are as defined, with the proviso that  $R^7$  is not attached to the 6-position comprising

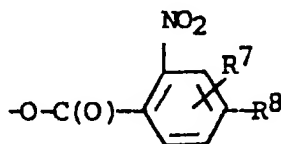
(a) reacting a dione of the formula



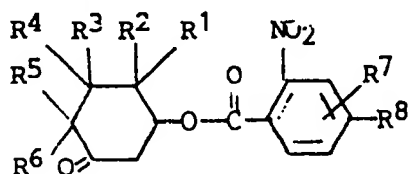
wherein  $R^1$  through  $R^6$  are as defined with a substituted benzoyl reactant of the formula



wherein  $R^7$  and  $R^8$  are as defined and  $X$  is halogen,  $C_1$ - $C_4$  alkyl- $C(O)-O-$ ,  $C_1$ - $C_4$  alkoxy- $C(O)-O-$  or

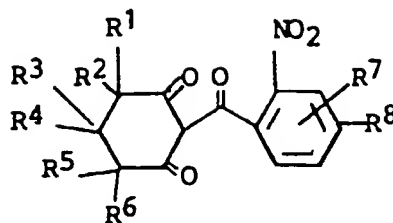


wherein  $R^7$  and  $R^8$  in this portion of the molecule are identical with those in the reactant shown above with at least a mole of a moderate base to form an enol ester of the formula



wherein  $R^1$  through  $R^8$  are as defined and in step (2) reacting a mole of the enol ester intermediate with 1 to 4 moles of a moderate base, and from 0.01 mole to about 0.5 mole or higher of a cyanide source to form a compound of the formula

0186118



wherein R<sup>1</sup> through R<sup>8</sup> are as defined above.

46. The process of Claim 45 wherein X is halogen, the moderate base is tri-C<sub>1</sub>-C<sub>6</sub> alkylamine, pyridine, alkali metal carbonate or alkali metal phosphate and the cyanide source alkali metal cyanide, cyanohydrins of methyl C<sub>1</sub>-C<sub>4</sub> alkyl ketones, cyanohydrins of benzaldehyde or C<sub>2</sub>-C<sub>5</sub> aliphatic aldehydes; cyanohydrins, zinc cyanide; tri(lower alkyl) silyl cyanides or hydrogen cyanide.

47. The process of Claim 46 wherein X is chlorine, the moderate base is tri-C<sub>1</sub>-C<sub>6</sub> alkylamine, pyridine, sodium carbonate or sodium phosphate and the cyanide source is potassium cyanide, acetone cyanohydrin or hydrogen cyanide.